Supporting information for: Room Temperature Lithium Phases from Density Functional Theory

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Phonon Density of States (PDOS)

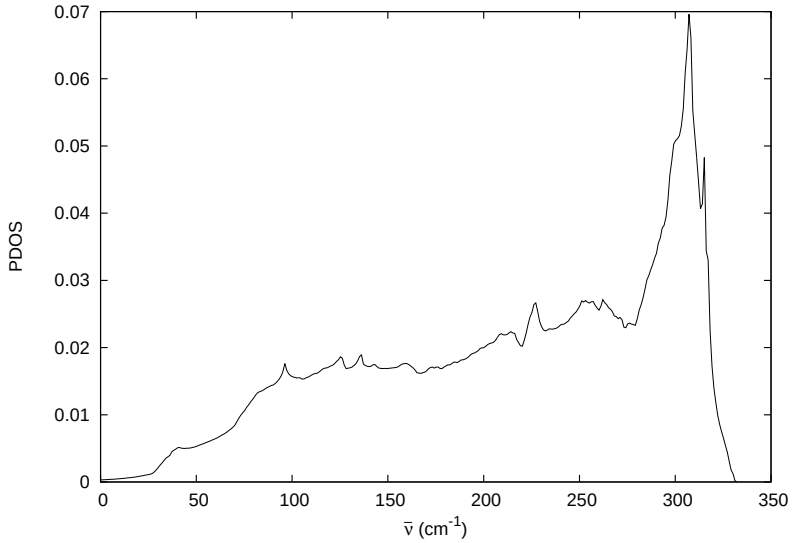

Figure S1: PDOS for bcc-Li computed as described in the main article.

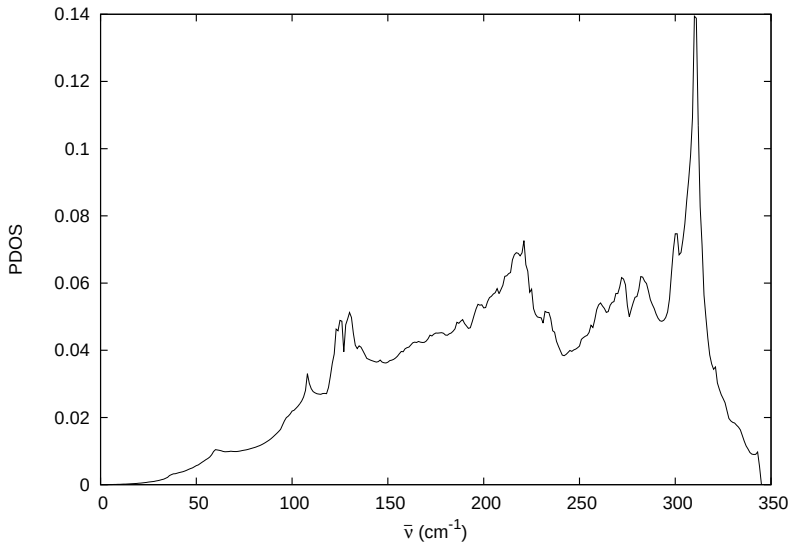

Figure S2: PDOS for fcc-Li computed as described in the main article.

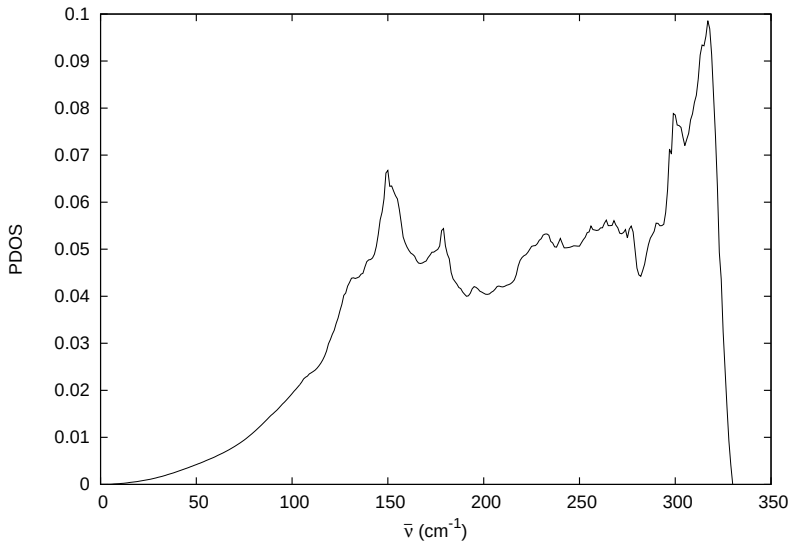

Figure S3: PDOS for hcp-Li computed as described in the main article.

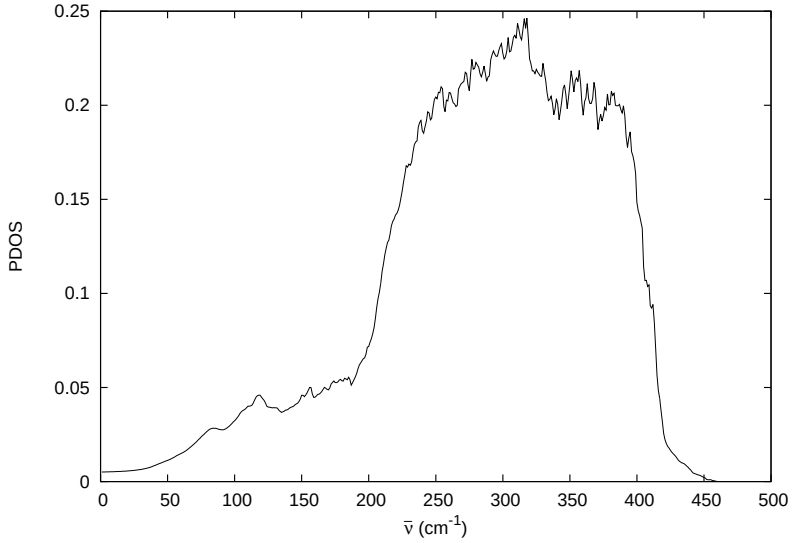

Figure S4: PDOS for cI16-Li computed as described in the main article.

Comparison of PBE and PBEsol

As reported in the main article, PBE predicts all four phases considered to be essentially degenerate. In order to assess whether this fact is accidental to PBE or the pseudopotential used, we computed bulk structures and energies for the same phases with a different pseudopotential (`pbesol-s-rrkjus_psl.0.2.1` from the Quantum Espresso database) and the functional

PBEsol, which is an evolution of PBE designed explicitly for solids.

As reported in the following Table, the two functionals predict essentially identical cell parameters and relative energies, with the exception of *hcp*: PBEsol predicts this phase to be slightly less stable.

Table S1: Results from PBE and PBEsol calculations at the optimized structures. Low temperature (0 K) cell parameters a and computed relative energies for the phases of Li considered. The ΔE do not contain ZPE or thermal corrections. A negative value indicates that the phase is more stable than *bcc*. Experimental relative energies are not available. See text in the main article for details.

	cell parameter a (Å)			computed ΔE (bcc=0.0)	
phase	**PBE**	**PBEsol**	**exp.**[a]	**PBE**	**PBEsol**
bcc	3.435	3.432	3.4615	0.0000	0.0000
fcc	4.324	4.321	4.328	-0.8066	-0.8422
hcp	3.058	3.058	3.069	-0.3859	34.8934
*cI*16	6.865	6.861	—	-0.0173	-0.0212

[a] 298 K data from ref. 20; 0 K extrapolation based on the *bcc* thermal expansion coefficient

Assuming the same ZPE and thermal corrections computed for PBE also apply to PBEsol, these values do not change the conclusions of the article.

Geometries

We report cell parameters and atomic positions for the bulk structures and the thickest slab considered for each surface. All values are in Ångström.

Bulk systems

```
BCC BULK: CELL PARAMETERS
```

```
     3.435000000   0.000000000   0.000000000
     0.000000000   3.435000000   0.000000000
     0.000000000   0.000000000   3.435000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000   0.0000000000
Li   1.717500000   1.717500000   1.7175000000


FCC BULK: CELL PARAMETERS
     4.324000000   0.000000000   0.000000000
     0.000000000   4.324000000   0.000000000
     0.000000000   0.000000000   4.324000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000   0.000000000
Li   0.000000000   2.162000000   2.162000000
Li   2.162000000   0.000000000   2.162000000
Li   2.162000000   2.162000000   0.000000000


HCP BULK: CELL PARAMETERS
     3.058000000   0.000000000   0.000000000
     0.000000000   5.296611371   0.000000000
     0.000000000   0.000000000   4.993693089
ATOMIC POSITIONS
Li   0.000000000   0.000000000   0.000000000
```

```
Li   1.529000000   2.648305673   0.000000000
Li   0.000000000   3.531074129   2.496846602
Li   1.529000000   0.882768455   2.496846602



CI16 BULK: CELL PARAMETERS
     6.865000000   0.000000000   0.000000000
     0.000000000   6.865000000   0.000000000
     0.000000000   0.000000000   6.865000000
ATOMIC POSITIONS
Li   0.052493154   0.052493154   0.052493154
Li   3.380016183   6.812505528   3.484994678
Li   6.812505528   3.484994678   3.380016183
Li   3.484994678   3.380016183   6.812505528
Li   1.768743188   1.768743188   1.768743188
Li   1.663763924   5.096246700   5.201236701
Li   5.201236701   1.663763924   5.096246700
Li   5.096246700   5.201236701   1.663763924
Li   3.484995268   3.484995268   3.484995268
Li   6.812509750   3.380015764   0.052487682
Li   3.380015764   0.052487682   6.812509750
Li   0.052487682   6.812509750   3.380015764
Li   5.201236824   5.201236824   5.201236824
Li   5.096247009   1.663756372   1.768751275
Li   1.768751275   5.096247009   1.663756372
Li   1.663756372   1.768751275   5.096247009
```

BCC slabs

```
BCC (100) -- 13 LAYERS: CELL PARAMETERS
     3.435000000   0.000000000   0.000000000
     0.000000000   3.435000000   0.000000000
     0.000000000   0.000000000  40.600000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000   0.032512951
Li   1.717500000   1.717500000  -1.750761436
Li   0.000000000   0.000000000  -3.432244570
Li   1.717500000   1.717500000  -5.147236831
Li   0.000000000   0.000000000  -6.876211948
Li   1.717500000   1.717500000  -8.577287122
Li   0.000000000   0.000000000 -10.305013127
Li   1.717500000   1.717500000 -12.032749225
Li   0.000000000   0.000000000 -13.733805236
Li   1.717500000   1.717500000 -15.462744193
Li   0.000000000   0.000000000 -17.177751911
Li   1.717500000   1.717500000 -18.859186259
Li   0.000000000   0.000000000 -20.642521091
```

```
BCC (110) -- 10 LAYERS: CELL PARAMETERS
     3.435000000   0.000000000   0.000000000
     0.000000000   4.857823585   0.000000000
     0.000000000   0.000000000  42.900000000
ATOMIC POSITIONS
```

```
Li   0.000000000   0.000000000  -0.052692526
Li   1.717500000   2.428911792  -0.052692449
Li   1.717500000   0.000000000  -2.383742897
Li   0.000000000   2.428911792  -2.383742188
Li   0.000000000   0.000000000  -4.841601796
Li   1.717500000   2.428911792  -4.841601817
Li   1.717500000   0.000000000  -7.289556812
Li   0.000000000   2.428911792  -7.289557659
Li   0.000000000   0.000000000  -9.718176260
Li   1.717500000   2.428911792  -9.718177636
Li   1.717500000   0.000000000 -12.142053327
Li   0.000000000   2.428911792 -12.142053675
Li   0.000000000   0.000000000 -14.570618745
Li   1.717500000   2.428911792 -14.570619174
Li   1.717500000   0.000000000 -17.018580216
Li   0.000000000   2.428911792 -17.018580056
Li   0.000000000   0.000000000 -19.476480564
Li   1.717500000   2.428911792 -19.476480160
Li   1.717500000   0.000000000 -21.807527028
Li   0.000000000   2.428911792 -21.807526296



BCC (211) -- 15 LAYERS: CELL PARAMETERS
     2.974797261   0.000000000   0.000000000
     0.000000000   4.857823585   0.000000000
     0.000000000   0.000000000  39.600000000
ATOMIC POSITIONS
```

```
Li  -0.108618927   0.000000000  -0.066761791
Li   1.105032995   2.428911792  -1.401716042
Li   1.973034736   0.000000000  -2.760436349
Li  -0.010599310   2.428911792  -4.186243786
Li   1.000568940   0.000000000  -5.571888887
Li   1.978643799   2.428911792  -7.027031080
Li  -0.001551451   0.000000000  -8.415755904
Li   0.991609865   2.428911792  -9.816388568
Li   1.984769067   0.000000000 -11.216819545
Li   0.004552061   2.428911792 -12.605692726
Li   0.982641128   0.000000000 -14.060745837
Li   1.993819881   2.428911792 -15.446489640
Li   0.010167707   0.000000000 -16.872124797
Li   0.878138073   2.428911792 -18.231008788
Li   2.091777739   0.000000000 -19.565848345



BCC (111) -- 21 LAYERS: CELL PARAMETERS
     4.857823585   0.000000000   0.000000000
     0.000000000   8.413997263   0.000000000
     0.000000000   0.000000000  38.800000000
ATOMIC POSITIONS
Li   0.000000000  -0.001352062   0.049915824
Li   2.428911792   4.205615057   0.049877471
Li   0.000000000   2.806614190  -1.179539831
Li   2.428911792   7.013740055  -1.179459632
Li   0.000000000   5.611065707  -1.846467689
```

Li	2.428911792	1.404012527	-1.846547366
Li	0.000000000	-0.002569525	-2.905553278
Li	2.428911792	4.204491493	-2.905560797
Li	0.000000000	2.804258516	-4.049216780
Li	2.428911792	7.011358054	-4.049163519
Li	0.000000000	5.607981389	-4.870660995
Li	2.428911792	1.400916947	-4.870692604
Li	0.000000000	-0.003910766	-5.936542033
Li	2.428911792	4.203113826	-5.936542969
Li	0.000000000	2.801777591	-6.996863927
Li	2.428911792	7.008850505	-6.996819123
Li	0.000000000	5.606650273	-7.882815309
Li	2.428911792	1.399558338	-7.882848567
Li	0.000000000	-0.000712670	-8.950468636
Li	2.428911792	4.206275545	-8.950431313
Li	0.000000000	2.803385183	-9.910857018
Li	2.428911792	7.010452973	-9.910813767
Li	0.000000000	5.608639136	-10.869827852
Li	2.428911792	1.401551952	-10.869853245
Li	0.000000000	0.001466940	-11.915623238
Li	2.428911792	4.208462771	-11.915582061
Li	0.000000000	2.806624827	-12.841355019
Li	2.428911792	7.013711001	-12.841306211
Li	0.000000000	5.613603841	-13.868659323
Li	2.428911792	1.406539675	-13.868691642
Li	0.000000000	0.002366580	-14.923440104
Li	2.428911792	4.209354283	-14.923418613

```
Li   0.000000000   2.806437304 -15.778599800
Li   2.428911792   7.013512469 -15.778552098
Li   0.000000000   5.613564856 -16.885471074
Li   2.428911792   1.406514071 -16.885526881
Li   0.000000000  -0.000392963 -17.936864139
Li   2.428911792   4.206621131 -17.936880607
Li   0.000000000   2.803833702 -18.622042161
Li   2.428911792   7.010924174 -18.621955873
Li   0.000000000   5.611180574 -19.837350889
Li   2.428911792   1.404065562 -19.837424556
```

```
BCC (120) -- 27 LAYERS: CELL PARAMETERS
     3.435000000   0.000000000   0.000000000
     0.000000000   7.680893500   0.000000000
     0.000000000   0.000000000  39.900000000
ATOMIC POSITIONS
Li   0.000000000  -0.260891312  -0.051590898
Li   1.717500000   2.232656868  -0.780619606
Li   0.000000000   4.711206895  -1.512686240
Li   1.717500000   7.025042605  -2.390820899
Li   0.000000000   1.602130990  -3.060369999
Li   1.717500000   3.870727846  -3.772485914
Li   0.000000000   6.157838674  -4.608895055
Li   1.717500000   0.782646481  -5.330487285
Li   0.000000000   3.084517342  -6.098225717
Li   1.717500000   5.379680555  -6.898442318
```

```
Li   0.000000000   0.020770276  -7.655999533
Li   1.717500000   2.321243602  -8.431089241
Li   0.000000000   4.620633813  -9.222339339
Li   1.717500000   6.912785939  -9.985155552
Li   0.000000000   1.524050672 -10.747964780
Li   1.717500000   3.823464053 -11.539184424
Li   0.000000000   6.123972252 -12.314337137
Li   1.717500000   0.765089445 -13.071905502
Li   0.000000000   3.060237052 -13.872108219
Li   1.717500000   5.362078122 -14.639821162
Li   0.000000000  -0.013108736 -15.361381793
Li   1.717500000   2.273964757 -16.197912387
Li   0.000000000   4.542570297 -16.909952925
Li   1.717500000   6.800580564 -17.579516616
Li   0.000000000   1.433495840 -18.457665695
Li   1.717500000   3.912052824 -19.189659217
Li   0.000000000   6.405552333 -19.918744396
```

FCC slabs

```
FCC (100) -- 10 LAYERS: CELL PARAMETERS
     4.324000000   0.000000000   0.000000000
     0.000000000   4.324000000   0.000000000
     0.000000000   0.000000000  39.500000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000  -0.005735105
Li   2.162000000   2.162000000  -0.005734350
Li   0.000000000   2.162000000  -2.151088255
```

```
Li   2.162000000   0.000000000  -2.151088255
Li   0.000000000   0.000000000  -4.328978334
Li   2.162000000   2.162000000  -4.328977964
Li   0.000000000   2.162000000  -6.489333807
Li   2.162000000   0.000000000  -6.489333807
Li   0.000000000   0.000000000  -8.649086965
Li   2.162000000   2.162000000  -8.649087041
Li   0.000000000   2.162000000 -10.808892190
Li   2.162000000   0.000000000 -10.808892190
Li   0.000000000   0.000000000 -12.968664069
Li   2.162000000   2.162000000 -12.968664415
Li   0.000000000   2.162000000 -15.129017261
Li   2.162000000   0.000000000 -15.129017261
Li   0.000000000   0.000000000 -17.306926040
Li   2.162000000   2.162000000 -17.306925900
Li   0.000000000   2.162000000 -19.452278396
Li   2.162000000   0.000000000 -19.452278396



FCC (110) -- 14 LAYERS: CELL PARAMETERS
     4.324000000   0.000000000   0.000000000
     0.000000000   6.115059444   0.000000000
     0.000000000   0.000000000  39.900000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000  -0.002518973
Li   0.000000000   3.057529722  -0.002518227
Li   2.162000000   1.528764945  -1.540560090
```

Li	2.162000000	4.586294499	-1.540560090
Li	0.000000000	0.000000000	-3.026333851
Li	0.000000000	3.057529722	-3.026334992
Li	2.162000000	1.528764643	-4.588451272
Li	2.162000000	4.586294801	-4.588451272
Li	0.000000000	0.000000000	-6.123950873
Li	0.000000000	3.057529722	-6.123952234
Li	2.162000000	1.528764358	-7.641658108
Li	2.162000000	4.586295086	-7.641658108
Li	0.000000000	0.000000000	-9.176852741
Li	0.000000000	3.057529722	-9.176852179
Li	2.162000000	1.528765884	-10.697100168
Li	2.162000000	4.586293560	-10.697100168
Li	0.000000000	0.000000000	-12.232261620
Li	0.000000000	3.057529722	-12.232263279
Li	2.162000000	1.528764662	-13.750010769
Li	2.162000000	4.586294782	-13.750010769
Li	0.000000000	0.000000000	-15.285504493
Li	0.000000000	3.057529722	-15.285504282
Li	2.162000000	1.528764557	-16.847585653
Li	2.162000000	4.586294887	-16.847585653
Li	0.000000000	0.000000000	-18.333383201
Li	0.000000000	3.057529722	-18.333383051
Li	2.162000000	1.528766085	-19.871429285
Li	2.162000000	4.586293359	-19.871429285

```
FCC (111) -- 9 LAYERS: CELL PARAMETERS
     3.057529722   0.000000000   0.000000000
     0.000000000   5.295796824   0.000000000
     0.000000000   0.000000000  39.900000000
ATOMIC POSITIONS
Li   0.000000000  -0.000064137  -0.058020101
Li   1.528764861   2.647838659  -0.058023402
Li   0.000000000   1.762310402  -2.454248877
Li   1.528764861   4.410212859  -2.454247651
Li   0.000000000   3.530873499  -4.980626666
Li   1.528764861   0.882974384  -4.980623180
Li   0.000000000   0.002336813  -7.485539438
Li   1.528764861   2.650235750  -7.485541857
Li   0.000000000   1.765259237  -9.985786187
Li   1.528764861   4.413159942  -9.985785400
Li   0.000000000   3.528198279 -12.486175823
Li   1.528764861   0.880297944 -12.486172829
Li   0.000000000  -0.000340363 -14.991078435
Li   1.528764861   2.647559507 -14.991077167
Li   0.000000000   1.768202429 -17.517473188
Li   1.528764861   4.416099701 -17.517468281
Li   0.000000000   3.530609111 -19.913705766
Li   1.528764861   0.882712163 -19.913710360
```

HCP slabs

```
HCP (0001) -- 9 LAYERS: CELL PARAMETERS
     3.058000000   0.000000000   0.000000000
```

```
     0.000000000   5.296611370   0.000000000
     0.000000000   0.000000000  39.970000000
ATOMIC POSITIONS
Li   0.000000000  -0.000176489  -0.057319198
Li   1.529000000   2.648130946  -0.057324907
Li   0.000000000   3.528572438  -2.453476138
Li   1.529000000   0.880265428  -2.453476674
Li   0.000000000   0.004780472  -4.982439256
Li   1.529000000   2.653088462  -4.982448699
Li   0.000000000   3.529229033  -7.487016914
Li   1.529000000   0.880922684  -7.487009645
Li   0.000000000  -0.000523634  -9.987368643
Li   1.529000000   2.647778570  -9.987372040
Li   0.000000000   3.529234132 -12.487793002
Li   1.529000000   0.880925326 -12.487792405
Li   0.000000000   0.004780627 -14.992283342
Li   1.529000000   2.653086079 -14.992290246
Li   0.000000000   3.528573538 -17.521297930
Li   1.529000000   0.880270937 -17.521296611
Li   0.000000000  -0.000172094 -19.917469715
Li   1.529000000   2.648133203 -19.917475837



HCP (10-10) -- 14 LAYERS: CELL PARAMETERS
     5.296611370   0.000000000   0.000000000
     0.000000000   4.993693089   0.000000000
     0.000000000   0.000000000  39.900000000
```

ATOMIC POSITIONS

Li	0.244655188	0.000000000	0.024960130
Li	3.286393807	2.496846544	0.024980884
Li	2.784784904	0.000000000	-1.594946628
Li	0.746276584	2.496846544	-1.594950083
Li	0.067704455	0.000000000	-3.067159684
Li	3.463369252	2.496846544	-3.067157947
Li	2.676621339	0.000000000	-4.600642114
Li	0.854456299	2.496846544	-4.600638151
Li	0.006611523	0.000000000	-6.116205311
Li	3.524489553	2.496846544	-6.116211192
Li	2.647701720	0.000000000	-7.650157845
Li	0.883378190	2.496846544	-7.650170303
Li	-0.004826585	0.000000000	-9.175311086
Li	3.535912588	2.496846544	-9.175319135
Li	2.643473075	0.000000000	-10.701630182
Li	0.887618096	2.496846544	-10.701629609
Li	-0.000597737	0.000000000	-12.226841910
Li	3.531666667	2.496846544	-12.226839016
Li	2.654926889	0.000000000	-13.760817843
Li	0.876169543	2.496846544	-13.760805851
Li	0.028319100	0.000000000	-15.276316724
Li	3.502764392	2.496846544	-15.276299624
Li	2.716004558	0.000000000	-16.809886580
Li	0.815053388	2.496846544	-16.809863296
Li	0.136481085	0.000000000	-18.282070497
Li	3.394579418	2.496846544	-18.282072935

```
Li   2.892990701   0.000000000 -19.902000399
Li   0.638061462   2.496846544 -19.901997069


HCP (11-20) -- 9 LAYERS: CELL PARAMETERS
     3.058000000   0.000000000   0.000000000
     0.000000000   4.993693089   0.000000000
     0.000000000   0.000000000  42.100000000
ATOMIC POSITIONS
Li   0.000000000   0.000000000  -0.016320022
Li   1.529000000   2.496846544  -0.973758315
Li   1.529000000   0.000000000  -2.568658734
Li   0.000000000   2.496846544  -3.567835335
Li   0.000000000   0.000000000  -5.264331455
Li   1.529000000   2.496846544  -6.200586416
Li   1.529000000   0.000000000  -7.925557280
Li   0.000000000   2.496846544  -8.829146807
Li   0.000000000   0.000000000 -10.578548485
Li   1.529000000   2.496846544 -11.490555107
Li   1.529000000   0.000000000 -13.240082934
Li   0.000000000   2.496846544 -14.143624664
Li   0.000000000   0.000000000 -15.868628507
Li   1.529000000   2.496846544 -16.804794962
Li   1.529000000   0.000000000 -18.501338238
Li   0.000000000   2.496846544 -19.500614227
Li   0.000000000   0.000000000 -21.095555711
Li   1.529000000   2.496846544 -22.052989159
```